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(54) Process for producing macro-
cyclic ester compounds

(57) A process for producing a macrocyclic ester compound comprises decomposing and cyclizing linear ester compounds, from high to low condensate, to the macrocyclic ester, with addition of glycol or oligo-ester compound of which the component is similar as those of the linear ester compounds. This addition makes the reaction easy and continuous, and improves its efficiency.

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SPECIFICATION

Process for producing macrocyclic ester compounds

- 5 The present invention relates to a process for producing macrocyclic ester compounds, especially a compound for use for musk perfume. 5

Macrocyclic ester compounds such as ethylene brassylate have a musk-like fragrance odour and are useful for musk perfume. As well known, these compounds are obtained in such a manner that the corresponded aliphatic dicarboxylic acid or its alkyl ester is reacted with
10 alkylene glycol, or otherwise the aliphatic dicarboxylic acid is reacted directly with alkylene oxide, to linear polyester and then the polyester is thermally depolymerized to monomeric units which are cyclized simultaneously. Usually, the cyclization reaction followed by thermal
15 depolymerization is carried out with heating under reduced pressure in the presence of catalyst. 10

However, according to various conventional techniques, mentioned above, this cyclization
15 reaction is accompanied by further polycondensation of the linear polyester and intermolecular crosslinking reaction in the reaction system. Consequently, the viscosity of the reaction content is raised to such an extent that its agitation is very difficult and its thermal conductivity is considerably reduced. As a result, the yield is decreased and a quality change of the macrocyclic
20 ester compound occurs. Moreover, decomposed gas is generated so that the odour and colour of the macrocyclic ester compound distilled from the reaction system are degraded. These
25 various defects are typical of the conventional methods. 20

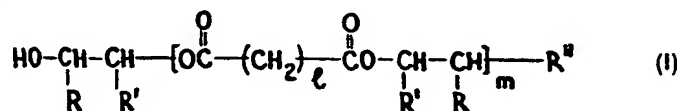
As one method for improving some of the defects mentioned above, the addition of an inert medium having a high boiling point to the reaction system to decrease the apparent viscosity has been disclosed in Japanese unexamined patent application No. 81875/1980, Japanese
25 unexamined patent application No. 56681/1978, and Japanese unexamined patent application No. 51472/1981. 25

The inert medium employable for above-mentioned process is liquid paraffin or solid paraffin. As is well known, this medium cannot dissolve the linear polyester and has only the effect of dispersing the high viscous polyester into the medium having a relatively low viscosity.
30 Consequently, in some cases, the polyester coagulates into large blocks and because of the use of a large amount of the medium the utility efficiency of the reactor is substantially reduced. 30
Moreover, the distilled macrocyclic ester compound is dissolved in the medium and its separation requires complicated operations.

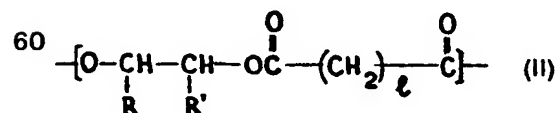
As another example of the method, mentioned above, a process for performing depolymerization and cyclization in the presence of polyoxyalkylene glycol and its derivative, monohydric
35 alcohol and its derivative or monovalent fatty acid and its derivative, either of which has high boiling point, is described in Japanese unexamined patent application No. 120581/1980. 35
According to this process, ether bonds of the added polyoxyalkylene glycol are decomposed and thereby various decomposed compounds are produced or decomposed gases are generated.
40 Consequently, a decrease in the degree of vacuum is brought about or the quality of the macrocyclic ester compound is degraded. In addition, the odour of the monohydric alcohol, the monovalent acid or derivatives thereof are mixed in the distillate and have a detrimental
45 influence on the odour of the macrocyclic ester compound from the viewpoint of its use as perfume. These phenomena were mentioned as defects of the conventional processes. 40

A process for producing a macrocyclic ester compound is also disclosed in Japanese patent
45 application No. 7279/1981. 45

According to the present invention there is provided a process for producing a macrocyclic ester compound, comprising the steps of adding glycol and/or oligo-ester compound having the
50 general formula: 50

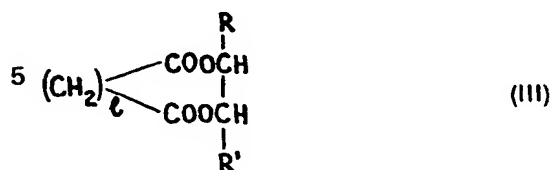


55 to a reaction system containing a linear ester compound having the general repeated unit formula: 55

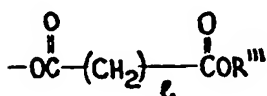


65 at an optional reaction stage so as to obtain a macrocyclic ester compound having the general 65

formula:



wherein R and R' both denote a hydrogen atom or one denotes a hydrogen atom and the other a methyl group or ethyl group, l is a positive integer in the range of 6 to 14, m is a positive integer indicating an average condensation degree in a range of zero to 20 or less, and R'' denotes hydroxy group or a group having the formula:

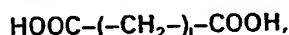


wherein R'' denotes a hydrogen atom or an alkyl group having 1 to 3 carbon atoms.

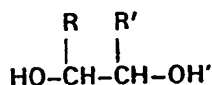
The resulting macrocyclic ester compound may be used for musk perfume.

By comparison with the process disclosed in Japanese patent application No. 7279/1981, even if a condensate having a low degree of condensation and being free from the peculiar physical properties in high polymers is used besides the conventional aliphatic polyester, in a process exemplifying the present invention the macrocyclic ester compound can be produced by means of adding the same kind of oligomer or the same kind of glycol to the reaction system. As the additive, mono-ester, di-ester or oligo-ester produced from the glycol and the dicarboxylic acid as components of the macrocyclic ester compound and/or glycol as one component of the said macrocyclic ester compound may be used without occurrence of the afore-mentioned disadvantages of the known methods.

In a process exemplifying the present invention, the linear ester compound represented by the general formula (II), as the raw material of the macrocyclic ester compound, can be produced by using conventional processes producing polyester. For example, dicarboxylic acid having the general formula:



or its ester, is reacted with glycol having the general formula:



if necessary, in the presence of a conventional catalyst, by means of an esterification reaction of ester exchange reaction to produce bis-glycol ester of the dicarboxylic acid or its polycondensate having lower degree of condensation. The bis-glycol ester or its polycondensate is heated to about 270°C, if necessary in the presence of a conventional polycondensation catalyst. As the reaction proceeds, the reaction system is kept under reduced pressure, finally 0.1 to 50 mmHg, and as the polycondensation proceeds the ester compound is produced.

As previously mentioned, the linear ester compound comprises those condensates ranging from lower molecular condensate, which does not indicate viscosity or elasticity peculiar to higher molecular polycondensate, to high molecular polycondensate having the above-mentioned physical properties. The condensation degree of the lower molecular condensate can be changed by the combination of dicarboxylic acid and glycol as raw materials. The lower molecular condensate obtained after the following stage of the reaction system is desirably used. The stage can be equal to the first step of a polyester polycondensation in which the reaction temperature is in the range of 230 to 260°C and the reaction pressure is in the range of 30 to 50 mmHg.

As the dicarboxylic acid there can be used suberic acid, azelaic acid, sebacic acid, n-namethylene-1,9-dicarboxylic acid, decamethylene-1,10-dicarboxylic acid (dodecanedioic acid), undecamethylene-1,11-dicarboxylic acid (brassylic acid), thapsic acid or the like. As ester of the acid there can be used dimethyl ester, diethyl ester or the like. A single acid type may be used, or a mixture of two or more acid types.

As the glycol there can be used, either singly or in a mixture of one or more, ~~ethylene~~ ethylene glycol, propylene glycol, 1,2-butylene glycol or the like.

In the conventional process for producing a macrocyclic ester compound represented by the general formula (III) from the linear ester compound, polycondensation of the linear ester compound is accelerated and after it reaches a high degree of polycondensation, an appropriate catalyst for depolycondensation and cyclization is added to the reaction system, depolymerization and cyclization then being carried out by heating under reduced pressure. Thus, the macrocyclic ester compound distilled outside the reaction system is collected and produced.

According to the conventional process, both depolymerization and cyclization reactions for producing the macrocyclic ester compound and the polycondensation reaction takes place competitively and thereby the degree of condensation of the polyester left in the reactor is substantially increased. Moreover, in addition to the two above-mentioned reactions, crosslinking reaction of the linear polyester occurs and after a while agitation becomes difficult. Furthermore, generation of the macrocyclic ester compound virtually stops and instead generation of other decomposed gas occurs.

On the other hand, according to a method exemplifying the present invention glycol and/or oligo-ester compound represented by the general formula (I) is or are added to the reaction system at the depolymerization and cyclization stage and thereby the degree of condensation of the linear ester compound in the reaction system is not raised above the necessary degree, so the crosslinking phenomenon does not take place from the initial to the final reaction stage. As a result, the macrocyclic ester compound can be generated continuously.

As a glycol and/or oligo-ester having the general formula (I), any reaction compound of the following glycol with the acid having a general formula: $\text{HOOC}-(\text{CH}_2)_l-\text{COOH}$ may be used in addition to ethylene glycol, propylene glycol, and 1,2-butylene glycol, a raw material of the linear ester compound, where l is a positive integer from 6 to 14. For example, as the oligomer having average degree of condensation of 20 or less, a monoglycol ester, bis-glycol ester or glycol carboxylate may be used. One kind of glycol or a mixture of two or more or the reaction product of the glycol with one kind or two or more of dicarboxylic acids may be used.

In carrying out a process according to a preferred example of the present invention, at first the linear ester compound is maintained in a molten state, with agitation and under reduced pressure of 50 mmHg or less with or without a catalyst, and as a result the same glycol as one component of the linear ester compound is initially distilled out. After a while the glycol distillation virtually terminates. After the stage when reaction pressure is decreased gradually to 0.1 to 1.0 mmHg, with addition of the catalyst if not added at the prior reaction stage, then both the macrocyclic ester compound and glycol are initially distilled out. As a result of the above distillation, the viscosity of the linear ester compound is substantially increased and agitation becomes gradually more difficult. The compound having the general formula (I) is then preferably added continuously or intermittently to the reactor, for example, from its bottom, in proportion to the distillation rate and thereby the macrocyclic ester compound and glycol are simultaneously distilled out without causing a further increase in the viscosity.

In the case of using the oligo-ester, the macrocyclic ester compound is continuously distilled out while the addition continues, but if necessary the reaction can be terminated at an optional stage.

In such a process various depolymerization and cyclization catalysts can be used for producing the macrocyclic ester compound from the linear ester compound represented by the general formula (II). For example, a lead compound including lead nitrate and lead borate, dialkyltin oxide, a complex catalyst containing an inorganic lead compound such as lead carbonate or lead sulfate with alkali metal, alkali earth metal or aluminium alkoxide, aluminium alkoxide only, aluminium compound having a carbonate radical, titanium alkoxide, or the like may be used.

The catalyst is preferably used in the range of 0.1 to 10 percent by weight of the dicarboxylic acid used as the raw material. The entire amount of the catalyst may be added to the reaction system at the same time the linear ester compound is charged, in which case a catalyst change at the addition of the glycol or oligo-ester is not necessary. Alternatively, a part of the catalyst amount may be added to the linear ester compound charged into the reaction system and the remaining part added to the glycol or oligo-ester. Thus, the catalyst may be added fully or partially at any time from the start of the linear ester compound reaction or the start of addition of the glycol or oligo-ester, or may be added to the linear ester compound or the glycol or oligo-ester, both prior to their addition to the reaction system. In all cases, the catalyst has the same effect on the depolymerization and cyclization reaction.

Macrocyclic ester compounds able to be produced by processes exemplifying the present invention are shown with IUPAC nomenclature as follows:

2,5-dioxa-1,6-dioxocycloalkane, 3-methyl-2,5-dioxa-1,6-dioxocycloalkane, 3,4-dimethyl-2,5-dioxa-1,6-dioxocycloalkane, 3-ethyl-2,5-dioxa-1,6-dioxocycloalkane or 3,4-diethyl-2,5-dioxa-1,6-dioxocycloalkane, in which the ring member is in the range of from 10 to 20.

Of these compounds, the cycloalkanes having from 12 to 17 ring members are preferred, especially:

- 2,5-dioxa-1,6-dioxocyclododecane (ethylene sebacate), 2,5-dioxa-1,6-dioxocyclohexadecane (ethylene dodecanedioate), 2,5-dioxa-1,6-dioxocycloheptadecane (ethylene brassylate), 2,5-dioxa-1,6-dioxocycloicosane (ethylene thapsate), 3-methyl-2,5-dioxa-1,6-dioxocyclohexadecane (propylene dodecanedioate) and 3-methyl-2,5-dioxa-1,6-dioxocycloheptadecane (propylene brassylate).

Through use of a process exemplifying the present invention, the utilization efficiency of the depolymerization and cyclization reactor can be enhanced and, if necessary, the above reaction step can be terminated at its optional stage. In the case of exhausting the reaction residue, the compound exemplified by the alkylene glycol as hereinbefore set forth is additionally added and thereby the residue is very easily decomposed, dissolved in the glycol and can be exhausted. This glycol solution can contain bis-glycol ester of the dicarboxylic acid same as the component of the linear ester compound having the general formula (II). Consequently, after filtering insoluble materials such as decomposed catalyst or others from the glycol solution, the bis-glycol in the solution can be utilized repeatedly as any part or all of the linear ester compound represented by the general formula (II). Even if a mechanism for the preferred effect is not cleared minutely, disproportionation or depolycondensation reaction will occur by adding the glycol and/or the oligo-ester and, as a result, agitation can be achieved easily and thermal conductivity improved without further raising the degree of polycondensation compared with conventional processes. Simultaneously, the depolymerization and cyclization will not necessarily require the polyester to have a sufficiently higher degree of condensation. Thus, even a linear ester compound having a very low degree of condensation can be used for the depolymerization and cyclization.

The distilled reaction product is rectified, if necessary, and thereby a macrocyclic ester compound having a high purity and desirably fragrant odour can be obtained. The macrocyclic ester compound can be produced from the linear ester compound with almost optimum viscosity and with a high yield and efficiency.

The glycol which is distilled out in producing the linear ester compound, in producing the macrocyclic ester compound or in the rectifying step may be reused.

Processes exemplifying the present invention will now be more particularly described with reference to the following Examples and Comparison Examples, in which all parts are parts by weight.

Example 1

(Process for producing linear ester compound)

244 parts of brassylic acid and 124 parts of ethylene glycol were charged into a reactor fitted with a distilling tower and an agitator, and the reactants were heated under agitation at ambient pressure.

The reaction temperature was maintained in the range of 150 to 220°C for three hours. After 35.7 parts of water had been distilled out, the reaction temperature was raised to 230°C and pressure was gradually decreased to 40 mmHg. The reaction was continued with heating and, when 48 parts of ethylene glycol had been distilled out, the reaction was terminated. The final temperature was 245°C.

The resulting product was low molecular weight condensate without tackiness in molten state.

(Process for producing macrocyclic ester compound)

142 parts of the above linear ester compound and 0.2 parts of dibutyl tin oxide were charged into the reactor for highly decreased pressure reaction with agitation. The reaction system was heated and the pressure was gradually reduced.

At 240°C and under 5 mmHg, both ethylene glycol and ethylene brassylate began to distil out. The ethylene glycol and ethylene brassylate separated into two layers in the receiving vessel. The lower layer (ethylene glycol) was separated out and continuously added to the bottom of the reactor in proportion to the amount of ethylene glycol which was distilling out.

During the period of this reaction, the temperature was kept in the range of 260 to 270°C and the agitator torque at 100 r.p.m. was almost constantly kept in the range of 1.5 to 2.0 kg-cm.

This reaction was continued for 8 hours whereby 129 parts of ethylene brassylate was produced, its yield relative to the used brassylic acid being 95.6%.

Comparison Example 1

In the above-mentioned process for producing the macrocyclic ester compound of Example 1, addition of the distilled ethylene glycol was not entirely achieved, the similar reaction being continued and thereby 10 parts of ethylene brassylate being distilled out during one hour. The torque at 100 r.p.m. was gradually raised and finally reached 9 kg-cm, the agitation then being

st pp d. The reaction without agitation was continued for 7 more hours, but the reaction mixture was crosslink d and coloured with its foaming and only 5 more parts of ethylene brassylat w re distilled out. Th total y ild was only 11.1% to th us d brassylic acid.

5 Example 2

5

(Process for producing oligomer for the addition use)

2,440 parts of brassylic acid and 1,340 parts of ethylene glycol were charged into a reactor fitted with a distilling tower and an agitator, and the reactants were heated in the range of 150 to 220°C for two hours, esterification being accelerated. After 355 parts of water had been
10 distilled out, the temperature was raised to 230°C and excess ethylene glycol was distilled out, oligomer then being produced. The average molecular weight of the oligomer was assumed to be about 400 from the amount of the glycol distilled and its hydroxy value. 10

(Process for producing a macrocyclic ester compound)

15 142 parts of the linear ester compound in Example 1 and 0.4 parts of lead nitrate were charged into a reactor fitted with an agitator and high vacuum means. The reaction system was gradually heated and kept at reduced pressure. At 240°C and 5 mmHg, distillation of both ethylene glycol and ethylene brassylate took place to a substantial degree and then the viscosity of the reaction system gradually increased. 15

20 In this stage, the oligomer mentioned above was entirely molten and was continuously added to the reactor from its bottom so as the amount of the reaction mixture was kept constant. During the period of this operation, the reaction temperature was kept in the range of 270 to 280°C and its pressure in the range of 0.5 to 2.0 mmHg. In addition, the viscosity of the reaction system was kept rather lower compared with that prior to the oligomer addition and
25 thereby both ethylene glycol and ethylene brassylate continuously distilled out. 25

The oligomer addition from initiation to termination required 25 hours and, after the termination of oligomer addition, the reaction was continued for two more hours at the same temperature and at the same pressure. Then the viscosity was raised such that agitation might become difficult and at this stage the reaction was finished.

30 The distilled amount of ethylene brassylate was 2,600 parts and its yield was 96.3% relative to the brassylic acid used. 30

Example 3

(Process for producing oligomer)

35 2,300 parts of dodecanedioic acid and 1,300 parts of ethylene glycol were charged into a reactor fitted with a distilling tower and an agitator and the reactants were heated in the range of 150 to 210°C for two hours for the esterification reaction. When 356 parts of water had been distilled out, its internal temperature was raised to 230°C and excess ethylene glycol was
40 distilled out, the average molecular weight of this oligomer being about 800. 40

(Process for producing macrocyclic ester compound)

280 parts of the oligomer were charged in a reactor fitted with an agitator and high vacuum means and the reaction system was gradually heated. When the oligomer had melted, 1.0 part of titanium tetrabutoxide was added in the reaction system, and with simultaneous agitation, the
45 reaction pressure was gradually reduced. At 240°C and under 5 mmHg, distillation of both ethylene glycol and ethylene dodecanedioate initiated to a substantial degree and the viscosity of the reaction system gradually increased. 45

Up to the time the pressure reached 0.7 mmHg, 23 parts of ethylene dodecanedioate had been distilled out. At this stage agitation became difficult, so the other parts of the oligomer
50 were melted and added to the reactor from its bottom. The pressure was retained at 0.3 to 0.7 mmHg and the temperature was kept at 280°C. This addition was continued so that the content weight would be kept constant. 50

The viscosity of the reaction system was lowered immediately after the oligomer addition, compared with that prior to the addition. The time required for the oligomer addition was 14
55 hours. 55

After the finish of this addition, the pressure was returned to ambient pressure and the reaction was immediately terminated, 2,260 parts of ethylene dodecanedioate being obtained.

The t mperatur w lowered to 220°C and 200 parts of ethylene glycol and 2 parts of sodium carbonat w re add d. Heating was continu d at less than r fluxing t mperatur for 3
60 hours and the r sidu al ster compound in the re ctor was decompos d and dissolved. Then a small amount of insolubl residu was filtered off and thereby ethylen glycol solution containing 284 parts f bis-hydroxyethyl ester of dodecanedioic acid was obtained. 60

Th yild of ethylene dod canedioate, which was calculated by taking into account the acid component of the bis-ester, was 97.0% relative to th dodecanedioic acid used.

Example 4

- 1.0 part of titanium tetrabutoxide was added to an ethylene glycol solution containing 284 parts of bis-hydroxyethyl ester of dodecanedioic acid in Example 3. The same reaction procedure mentioned in the process for producing macrocyclic ester compound in Example 1 was carried out and thereby 220 parts of ethyl dodecanedioate were obtained in a yield of 95.4% of the used acid component.

Comparison Example 2

- The coloured, crosslinked residue remaining in the reactor after the reaction in Comparison Example 1 was slightly cooled and 100 parts of ethylene glycol and 1.0 part of sodium carbonate were added to the reactor at 210°C. As a result, the residue gradually decomposed and, after 4 hours, ethylene glycol solution containing a large amount of insoluble material was obtained. The insoluble material was filtered off and ethylene glycol solution containing 136 parts of bis-hydroxyethyl ester of brassylic acid was obtained.
- To this ethylene glycol solution, 0.2 parts of dibutyl tin oxide were added and the same reaction as described in Comparison Example 1 was carried out. Thereby, 7.6 parts of ethylene brassylate were obtained in a yield of 6.9% relative to the used brassylic acid.

Example 5

- (Process for producing oligomer)
- 1,010 parts of sebacic acid and 620 parts of ethylene glycol were used and the same process for producing oligomer in Example 3 was carried out. Oligomer was obtained with an average molecular weight of about 500.
- (Process for producing macrocyclic ester compound)
- 230 parts of the oligomer was charged into a reactor fitted with an agitator and high vacuum means and the reaction system was gradually heated. 0.5 parts of titanium tetrabutoxide were added. By agitation, pressure was gradually reduced and at 240°C and under 4 mmHg, distillation of both ethylene glycol and ethylene initiated to a substantial degree. At the same time, the viscosity began to increase and the rest of the oligomer mentioned above was melted and added continuously to the reactor from its bottom for 5 hours under reduced pressure, so that a constant amount was kept. During the period of the reaction, pressure was kept at 0.3 to 0.7 mmHg and temperature was maintained at 280°C.
- After the addition had finished, the same temperature and the same pressure were maintained for two more hours. An amount of ethylene sebacate was distilled, but the viscosity was raised to such an extent that its agitation became impossible. Pressure was therefore returned to ambient pressure and the reaction was stopped.
- 910 parts of ethylene sebacate were obtained and its yield relative to the used sebacic acid was 97.3% according to the similar calculation as mentioned in Example 3.
- The residue in the reactor was able to be reused.

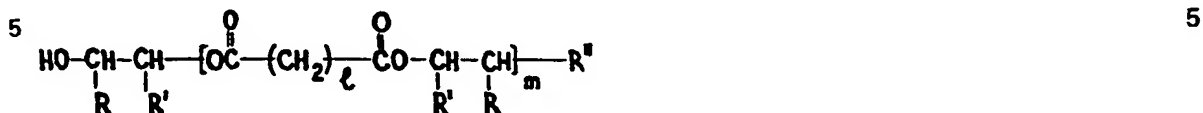
Example 6

(Process for producing the oligomer)

- 1,150 parts of dodecanedioic acid, 760 parts of propylene glycol and 1.5 parts of titanium tetrabutoxide were charged into a reactor fitted with a distilling tower and an agitator. The reactants were heated in the range of 150 to 200°C and about 36 parts of water were distilled out. Afterwards, an excess of propylene glycol was distilled out at 210 to 220°C and thus the oligomer was produced. The average molecular weight of the oligomer was about 550.
- (Process for producing macrocyclic ester compound)
- 280 parts of the oligomer were charged into a reactor fitted with an agitator and high vacuum means. The reactants were gradually heated and pressure gradually reduced with agitation. At 240°C and under 3 mmHg, distillation of both propylene glycol and propylene dodecanedioate was initiated to a substantial degree.
- In the meantime, the distillation was continuously carried out. As viscosity increased gradually, and the temperature raised to 260°C and pressure decreased to the range of 0.3 to 0.5 mmHg, then the remainder of the oligomer produced was melted and added continuously to the reactor for 25 hours, so that the content amount was kept constant and thereby propylene dodecanedioate was continuously produced.
- After the addition was finished, the reaction was continued for one more hour. Agitation then became impossible. Pressure was therefore returned to ambient and the reaction terminated.
- 1,094 parts of propylene dodecanedioate were obtained. The yield was 98.8% relative to the dodecanedioic acid used with the same measurement in Example 3, which took into account the dodecanedioic acid remaining in the reactor.

CLAIMS

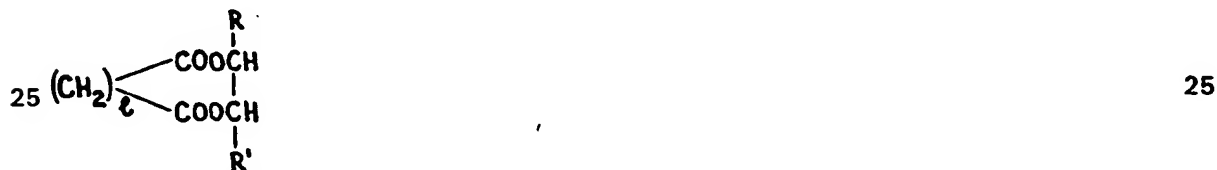
1. A process for producing a macrocyclic ester compound, comprising the steps of adding at least one of glycol and oligo-ester compound having the general formula:



10 to a reaction system containing a linear ester compound having the general repeated unit formula:



20 at an optional reaction stage so as to obtain a macrocyclic ester compound having the general formula:



30 wherein R and R' both denote a hydrogen atom or one denotes a hydrogen atom and the other a methyl group or ethyl group, l is a positive integer in the range of 6 to 14, m is a positive integer indicating an average condensation degree in a range of zero to 20 or less, and R'' denotes a hydroxy group or a group having the formula:



40 wherein R''' denotes a hydrogen atom or an alkyl group having 1 to 3 carbon atoms. 40

2. A process for producing a compound as claimed in claim 1, wherein R and R' both denote a hydrogen atom and l is a positive integer in the range of 6 to 11.

3. A process substantially as hereinbefore described with reference to any one of Examples 1 to 6.

45 4. A compound when produced by a method as claimed in any one of the preceding claims. 45